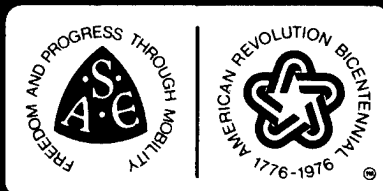


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# Stress Cracking of Plastics by Gasoline

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GLASSY THERMOPLASTICS are known to be highly susceptible to environmental stress cracking when exposed to organic liquids. This type of failure can be prevented by insuring that the level of mechanical stress on the plastic is below the characteristic critical cracking stress for the particular liquid environment. The mechanism by which liquid contact initiates craze or crack formation is not presently known; however, several authors (1-5)\* have shown that critical stress can be correlated with the solubility of the liquid in the polymer. Values of critical stress and critical strain have been reported in the literature for a variety of glassy plastics exposed to pure liquids (1-9); however, the stress cracking behavior of liquid mixtures has received little attention.

The present investigation was initiated to determine the susceptibility of glassy polymers to cracking when exposed to gasolines or mixtures of gasoline components. The objectives were to measure the range of critical stresses for polycarbonate (PC), poly(methyl methacrylate) (PMMA), and cellulose acetate butyrate

(CAB) in contact with gasolines, to define the effect of chemical composition on critical stress, and to develop methods for predicting the stress cracking characteristics of complex liquid mixtures from the physical constants of the pure liquid components.

## EXPERIMENTAL

Tensile specimens conforming to ASTM D638, type I, were injection molded using standard processing conditions. Materials employed were the three plastics mentioned above, namely, polycarbonate, cellulose acetate butyrate, and poly(methyl methacrylate).

Critical strains were measured using two pieces of apparatus. A three point bending form (8) instrumented to continuously monitor strain was used to measure the time for craze initiation at various fixed initial strains. All other critical strain data were obtained using an elliptical bending form (10) having a strain distribution of 0.3% to 2.3%. Critical stresses were calculated by multiplying the measured critical strains by the appropriate tensile modulus.

A precisely measured 5 ml quantity of test fluid was poured onto the stressed surface and

\*Numbers in parentheses designate References at end of paper.

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## ABSTRACT

The susceptibility of polycarbonate, poly(methyl methacrylate), and cellulose acetate butyrate to gasoline-induced stress cracking was evaluated by measuring the critical strains of specimens exposed to a variety of commercial gasolines and gasoline components. In general, the critical strain decreased and the severity of cracking of molded parts increased as the aromatic content of the gasolines increased.

However, low molecular weight aliphatics as well as specific aromatic components did also markedly reduce critical strain. The effects of sample geometry, temperature, and weathering on critical strain were determined. The capability to predict the critical strain of polymers in the presence of complex liquid mixtures on the basis of physical constants of pure liquid components was examined.

the critical strain was established after a ten minute period. Edge initiated crazing was prevented by coating the edges with a gasoline resistant grease. Values reported in this study represent an average of 3 to 10 separate measurements for each test liquid.

Gasoline samples were obtained locally in the Detroit area. Gasoline components, 99 mole percent pure, were obtained from the Phillips Petroleum Company.

## RESULTS AND DISCUSSION

**EFFECT OF TIME AND GEOMETRY** - Stress cracking characteristics of polycarbonate (PC), poly(methyl methacrylate) (PMMA), and cellulose acetate butyrate (CAB) were evaluated by measuring the minimum strain required to crack or craze samples exposed to gasolines or gasoline components. The time dependency of the crazing phenomena was determined using the three point bending form. Crazing strains are presented in Figure 1 for polycarbonate samples exposed to iso-octane, toluene, and a mixture of these two gasoline components. Iso-octane is a mild crazing agent; while toluene causes severe cracking of polycarbonate. Each of the two pure liquids and the mixture exhibit a characteristic critical strain below which crazing or cracking is not observed for exposure times of up to one hour. Since the critical strain is reached in a few minutes, a ten minute exposure was chosen for measurements on the elliptical bending form.

Critical strains for the entire range of toluene/iso-octane mixtures measured on the elliptical bending form are presented in Figure 2 for polycarbonate and in Figure 3 for poly(methyl methacrylate). Values of critical strain are shown for edge initiated crazes as well as for samples whose edges were coated with grease to prevent edge crazing. It is apparent from these figures that sharp edges have a significant effect on the measured values of critical strain and that poly(methyl methacrylate) appears to be more susceptible to edge initiated crazing than polycarbonate. From a design standpoint, sharp edges and corners should be avoided when gasoline cracking is a possibility. Subsequent measurements of critical strains for gasolines were performed on samples with coated edges to minimize the influence of geometrical factors on critical strain.

**EVALUATION OF STRESS CRACKING OF MOLDED PARTS** - Stresses which contribute to environmental stress cracking of molded parts include residual molding stresses, stresses from assembly operations such as mechanical attachment, and stresses which the part encounters in service. When the combined stresses are above a critical level, crazing or cracking of the part will occur. For parts with complex geometries, the stress distribution, molecular orientation, and geometrical factors generally result in a complex crazing and cracking pattern when the

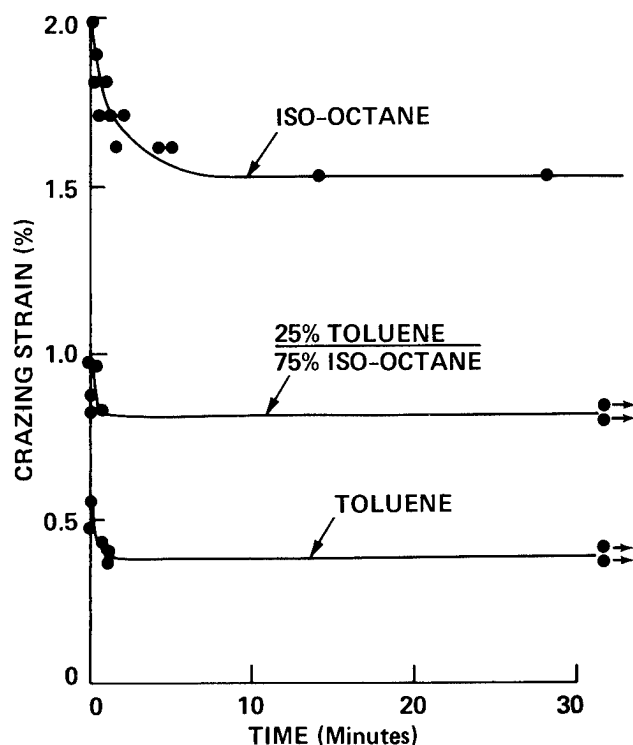


Fig. 1 - Crazing strain as a function of time of polycarbonate exposed to iso-octane, toluene, and a mixture of these two liquids

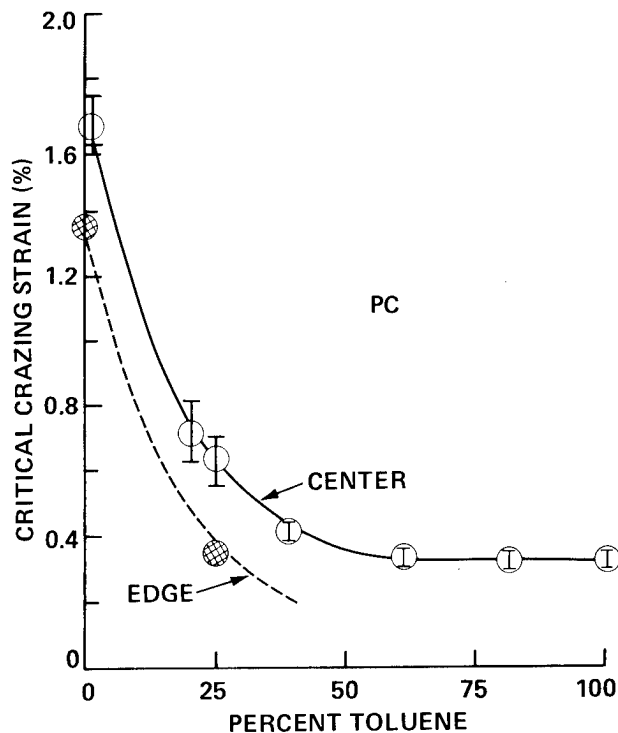


Fig. 2 - Critical strains of polycarbonate exposed to toluene/iso-octane mixtures

part is exposed to a crazing agent. It is important to establish a correlation between critical strains measured on geometrically simple test samples and the severity of environ-

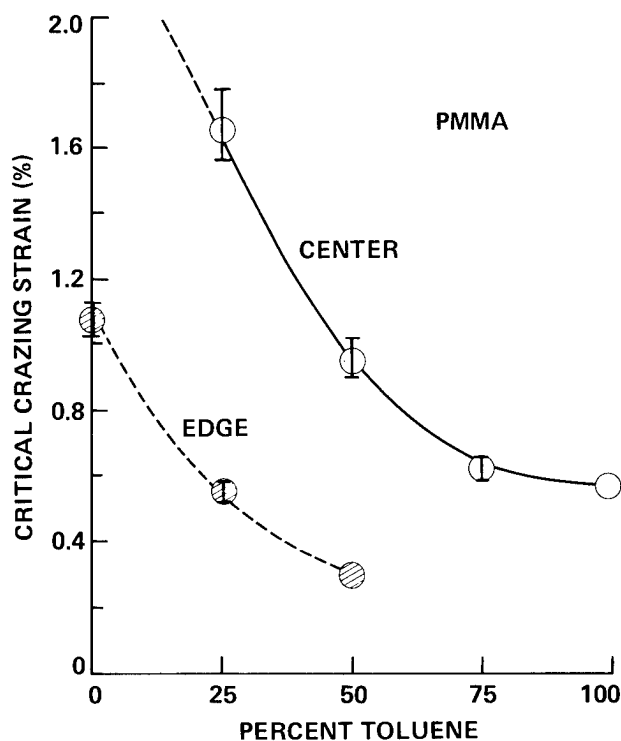


Fig. 3 - Critical strains of poly(methyl methacrylate) exposed to toluene/iso-octane mixtures

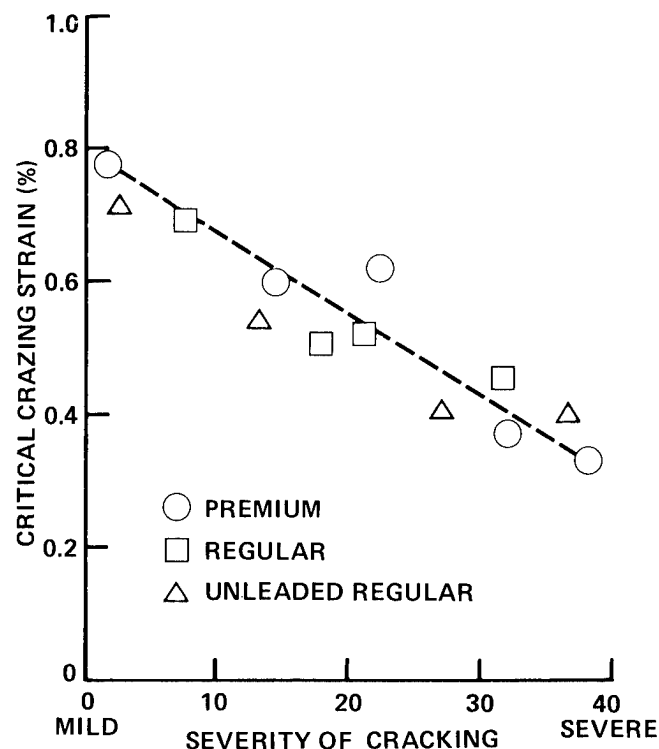


Fig. 4 - Critical strain as a function of severity of cracking of complex polycarbonate parts exposed to gasolines

mental stress cracking observed in complex parts.

Critical strains of polycarbonate exposed to thirteen commercial gasolines are presented as a function of severity of cracking of complex molded parts in Figure 4. Critical strains were measured on the elliptical bending form and are summarized for each of the gasolines in Table 1. Severity of cracking was determined by visually ranking parts exposed to each of the gasolines. As shown in Figure 4, there is an excellent correlation between severity of cracking and critical strain.

**EFFECT OF GASOLINE COMPOSITION** - Critical strains and critical stresses for polycarbonate and poly(methyl methacrylate) exposed to a variety of commercial gasolines as well as the overall composition of each of the gasolines are presented in Tables 1 and 2. Critical strains for both materials decrease as the aromatic content of the gasolines increases. This is most clearly shown in Figure 5. Poly(methyl methacrylate) exhibited a greater resistance to gasoline-induced crazing and/or cracking than polycarbonate as shown by its higher values of critical strain. Cellulose acetate butyrate was not cracked or crazed by any of the gasolines at strains as high as two percent. No correlation was observed between critical strain and gasoline type, i.e., premium, regular, or unleaded.

Although there was a general correlation between critical strain and aromatic content of commercial gasolines, a detailed compositional analysis of selected gasolines suggested that

Table 1 - Critical Strains and Stresses for Polycarbonate Exposed to Commercial Gasolines

Gasoline	Grade	Percent Aromatic	Critical Strain, Percent	Critical Stress, MPa (PSI)
A	Premium	9	0.78	17.5 (2540)
B	Unleaded	14	0.72	16.1 (2340)
C	Regular	18	0.69	15.4 (2240)
D	Premium	20	0.62	14.1 (2050)
E	Premium	23	0.60	13.4 (1950)
F	Unleaded	23	0.54	12.1 (1760)
G	Regular	26	0.53	11.8 (1720)
H	Regular	25	0.46	10.3 (1500)
I	Regular	21	0.45	10.1 (1460)
J	Unleaded	26	0.40	9.0 (1300)
K	Unleaded	25	0.40	9.0 (1300)
L	Premium	29	0.37	8.3 (1200)
M	Premium	48	0.33	7.3 (1060)

Table 2 - Critical Strains and Stresses for Poly(Methyl Methacrylate) Exposed to Commercial Gasolines

Gasoline	Grade	Percent Aromatic	Critical Strain, Percent	Critical Stress, MPa (PSI)
A	Premium	9	1.91	67 (9700)
G	Regular	26	1.46	51 (7400)
M	Premium	48	0.87	30 (4400)

specific aromatic as well as low molecular weight aliphatic components tended to reduce critical strain. In order to determine the effect of individual gasoline components on critical strain, artificial gasoline mixtures consisting of 75% aliphatic and 25% aromatic components by volume were tested. As shown in

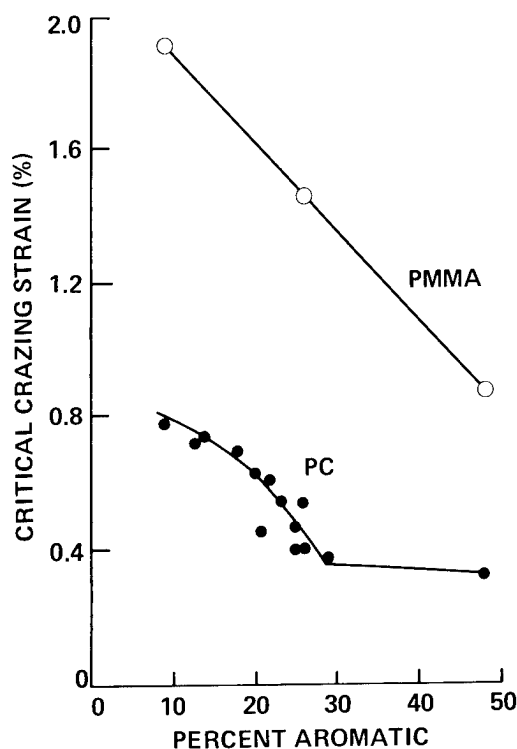


Fig. 5 - Critical strains of polycarbonate and poly(methyl methacrylate) as a function of gasoline aromatic content

Table 3, a low molecular weight aliphatic hydrocarbon significantly reduces critical strains of both polycarbonate and poly(methyl methacrylate). These results are consistent with the literature (11,12) in that increasing molecular weight or branching decreases sorption equilibria and sorption rate. Contrary to expected results, however, crazing strains appear to decrease as the molecular weights of aromatic components of the mixture increase. The absorption characteristics of these mixtures are currently being determined.

**PREDICTION OF CRITICAL STRAINS OF COMPLEX MIXTURES** - Critical strains of polycarbonate, poly(methyl methacrylate), and cellulose acetate butyrate exposed to pure components of gasoline are summarized in Table 4. Poly(methyl methacrylate) exhibits uniformly higher critical strains than polycarbonate when exposed to aliphatic or aromatic hydrocarbons. Although cellulose acetate butyrate was swollen by the aromatics, this material was not cracked or crazed by any of the gasoline components at strains of up to two percent.

Several authors (1,7-9) have shown correlations between critical strain and liquid parameters such as penetrant size, surface tension, solubility parameter, and hydrogen bonding parameter. Critical strains of polycarbonate are plotted as a function of solubility parameter and hydrogen bonding parameter for a broad range of organic liquids in Figure 6. Critical strains for liquids which are not gasoline components were taken from the liter-

Table 3 - Critical Strains for Plastics Exposed to Artificial Gasoline Mixtures

Liquid Mixture	PC		PMMA	
	Critical Strain, Percent	Critical Stress, MPa (PSI)	Critical Strain, Percent	Critical Stress, MPa (PSI)
25% Toluene + 75% Iso-octane 75% N-Pentane	0.65 0.34	14.5 (2110) 7.6 (1110)	1.56 0.63	55 (7960) 22 (3210)
75% Iso-octane + 25% Benzene	0.84	18.8 (2730)	1.85	65 (9430)
25% Toluene	0.65	14.5 (2110)	1.56	55 (7960)
25% O-Xylene	0.36	8.0 (1170)	1.12	39 (5710)
25% Ethyl Benzene	0.35	7.9 (1140)	0.94	33 (4800)
25% 1,2,4 Trimethyl Benzene	0.40	9.0 (1300)	1.56	55 (7960)

Table 4 - Critical Strains for Plastics Exposed to Gasoline Components

Liquid	Critical Strain (%)		
	PC	PMMA	CAB
<b>Aliphatics</b>			
1-Pentene	0.77		
N-Pentane	0.85	1.66	>2
N-Heptane	0.89		
N-Octane	0.99	>2	
Iso-Pentane	1.15		
Iso-Octane	1.66	>2	>2
<b>Aromatics</b>			
Benzene	<0.3	1.0	>2
Toluene	0.3	0.63	
O-Xylene	<0.3	0.88	
Ethyl Benzene	<0.3	0.60	
1,2,4-Trimethyl Benzene	0.3	1.0	>2
<b>Others</b>			
Methanol	1.19	0.65	>2
Nitromethane	0.69	>0.3	>2

ature (2,9). The solubility map in Figure 6 predicts critical strains for gasolines to range from 0.35% to 1.0%, which is approximately what was observed experimentally. However, the solubility mapping technique does not account for differences in the critical strains for individual aliphatic components, nor does it adequately account for the effects of different aromatic components on the critical strains for artificial gasoline mixtures. The difficulty of quantitatively predicting critical strains for complex mixtures is illustrated in Figures 2 and 3. The critical strains for these mixtures are not defined by simple functions of the critical strains for the pure liquid components. In conclusion, methods presently available for predicting critical strains for pure liquids from liquid properties may be used successfully as a guide for estimating critical strains for complex mixtures, but direct measurements of solubility appear to be necessary to fully account for the critical strain behavior in liquid mixtures.

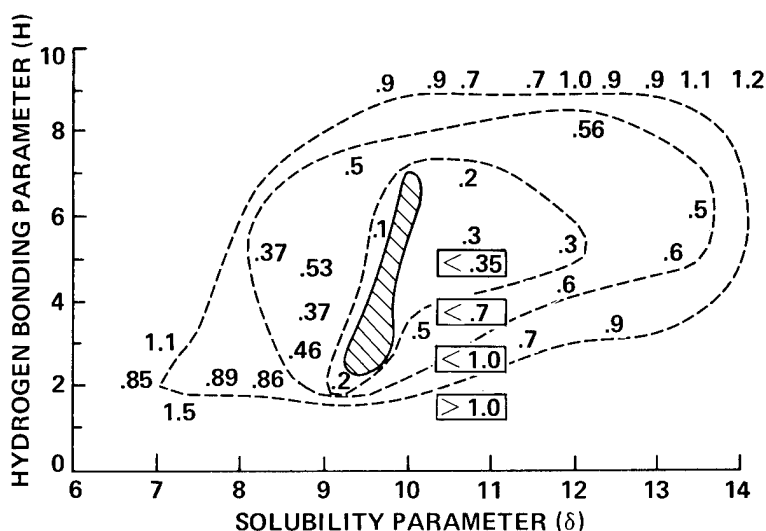


Fig. 6 - Critical strains of polycarbonate exposed to a variety of pure liquids as a function of liquid solubility parameter and hydrogen bonding parameter

#### SUMMARY

The susceptibility of polycarbonate (PC), poly(methyl methacrylate) (PMMA), and cellulose acetate butyrate (CAB) to gasoline-induced stress cracking was evaluated by measuring the critical strains of specimens exposed to a variety of commercial gasolines and gasoline components. Critical strains of these materials exposed to gasolines are as follows:

PC:	0.3 to 0.8%
PMMA:	0.8 to 1.9%
CAB:	>2.0%

Geometrical factors, such as sharp edges, reduced critical strain significantly. A general correlation was observed between the aromatic content of the gasolines and critical strain. However, low molecular weight aliphatic as well as specific aromatic components markedly reduced the critical strains of gasolines. No correlation was observed between critical strain and gasoline type, i.e., premium, regular, or unleaded.

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